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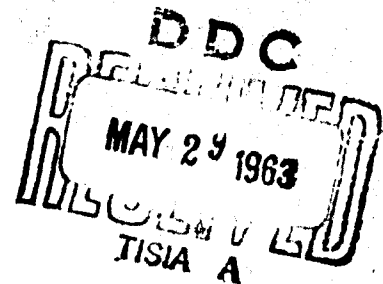
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RADIATION POLYMERIZATION OF ACETYLENE DERIVATIVES

2 October 1962 - 2 April 1963
Contract No. H068-88160

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FINAL REPORT

MRC BA-16

(2)
RADIATION POLYMERIZATION OF ACETYLENE DERIVATIVES

2 October 1962 - 2 April 1963
Contract No. N0bs-88166

Project Serial No. R007 1101, Task 0554

OBJECT

Investigate the radiation-induced polymerization of acetylene derivatives as a means of preparing high polymers that are thermally stable and useful as semiconductors.

AUTHORS

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26 April 1963

FOREWORD

This research study, covering the period 2 October 1962 to 2 April 1963, was conducted for the Bureau of Ships, Department of the U. S. Navy, under Contract No. N0bs-88166. The investigation is a continuation of the research study previously conducted from 10 August 1961 to 10 August 1962 for the Bureau of Ships under Contract No. N0bs-86072.

The research was conducted at the Dayton Laboratory, Monsanto Research Corporation, with Dr. W. H. Yanko as project engineer.

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RADIATION POLYMERIZATION OF ACETYLENE DERIVATIVES

I. PURPOSE

The primary purpose of these studies was to investigate the radiation-induced polymerization of selected acetylene derivatives as a means of preparing high polymers that potentially are thermally stable and useful as semiconductors. Fulfilling this major objective included synthesizing specific monomers, polymerization and copolymerization studies, chemical and physical alteration of high polymers produced to effect improvement in electrical properties, and a study of products obtained from radiation-sensitive acetylene derivatives to establish conditions for producing high molecular weight polymers.

Secondary objectives included correlation of chemical structure with radiation sensitivity and an increased understanding of the mechanism of radiation-induced chemical reactions.

II. SUMMARY

Research on the radiation-induced polymerization of acetylene derivatives to produce polyene polymers with useful properties concerned synthesis of acetylene derivatives, thermal, chemical and radiation-induced polymerizations and copolymerizations of selected acetylene derivatives, and characterization and evaluation of the prepared polymers.

Diethynylbenzenes were prepared and used as crosslinking agents in these polymerizations to insure solid products. Five acetylene compounds were prepared for these studies and the syntheses of four others were attempted unsuccessfully. A total of 17 radiation-induced polymerizations and copolymerization of various acetylenic systems were conducted during this study. Radiation yields with G values (number of monomer molecules polymerized per 100 ev of absorbed radiation) greater than 100 were observed in the copolymerizations of p-diethynylbenzene/propionic acid (296) and p-diethynylbenzene/dimethylethynylboronate (136) systems. Radiation yields for the polymerization and copolymerization of all other acetylene derivatives except propionic acid were small and G values were less than 30. In general, the systems examined were thermally sensitive which necessitated low temperature radiolyses to determine radiation yields.

Two polymeric systems, p-polyphenyl and polyferrocene, which should have long conjugated paths were prepared chemically and included in this study.

The polymers prepared were mostly highly colored and solid, indicating high molecular weight. The solid polymers were evaluated for resistivity values and disappointingly high values, over 10^{10} ohm-cm, were obtained. Traces of water in the polymers containing polar groups, greatly improved the conductivity of the polymers. Conversion of the basic and carboxylic acid functional groups on formed polymers to their hydrochloride and metal salts respectively, did not significantly lower the electrical resistivity of the polymers.

III. FACTUAL DATA

A. DISCUSSION

1. Background

The radiation-induced polymerization of acetylene derivatives was undertaken as a means of producing polyene polymers that might have unique and useful properties. In general, long chain polyenes with uninterrupted conjugation are expected to be thermally stable and to have semiconducting properties that could lead to practical applications.

The first year's work (1), of which this study is an extension, was encouraging with respect to the radiation-sensitivity of many acetylenic monomers to polymerization. However, the polymers formed were not suitable for semiconduction application due to their low molecular weight and high resistivity values. The current study was undertaken to effect improvement of the molecular weight of fully conjugated acetylenic polymers by use of diethynyl aromatic compounds as crosslinking agents. Also characterization of low molecular weight products derived from the polymerization of radiation sensitive monomers such as propiolic acid could lead to the definition of possible methods for increasing the polymer molecular weight.

In addition, improvements in polymer electrical properties was planned by building in functional groups in the side chain to modify the electronic behavior of the polyene backbone.

2. Acetylenic Derivative Preparation

Five acetylenic materials were synthesized for use in radiation polymerization studies. Two diethynyl compounds, p- and m-diethynylbenzene, were prepared for use as a monomer in homopolymerizations and as a comonomer in copolymerizations which should increase molecular weight and conjugation paths in the

resulting polymers. Other acetylenic compounds prepared were dicyanoacetylene, phenylchloroacetylene, and dimethylethynylboronate. In addition to the above monomers, p-polyphenyl and polyferrocene were synthesized from benzene and ferrocene, respectively.

p- and m-Diethynylbenzene were prepared from divinylbenzene via bromination and subsequent dehydrobromination. The synthesis of the para-isomer was repeated five times using from 0.6 to 2.9 mole of mixed divinylbenzenes (a mixture of 40% m- and 40% p-divinylbenzene along with ethylvinyl- and diethylbenzene). Yields of both isomers were poor (para- 5% and meta- 2.5%) due to the impure starting material, decomposition of the products during bromination and work-up, and incomplete product isolation.

From previous studies dicyanoacetylene, phenylchloroacetylene, dimethylethynylboronate, cyanophenylacetylene, cyanophenylpropionic acid, and diethynylanthracene were selected as potentially fruitful monomers for polymerization to polyenes via radiolysis. These monomers were expected to be sensitive to radiation-induced polymerization and to produce solid high molecular weight polymers. In addition, the cyano-monomers would provide the polymer with reactive functional groups which could be chemically converted to various derivatives. Correlation of polymer electrical property changes in such derivatives could direct future studies to promising semiconductor materials.

The attempted syntheses of o-cyanopropionic acid and o-cyanophenylacetylene from the corresponding cinnamic acid repeatedly yielded tars. Attempts to react sodium phenylacetylide with cyanogen bromide to produce phenylcyanoacetylene was unsuccessful yielding only starting materials. Several attempts to reduce the 9,10-diethynyl-9,10-dihydroanthraquinol, prepared from anthraquinone, to the corresponding diethynylanthracene with stannous chloride failed.

Dicyanoacetylene was prepared via amidation of dimethyl acetylenedicarboxylate (80% yield) and subsequent P_2O_5 -dehydration to the corresponding nitrile (11% yield). Phenylchloroacetylene was prepared by the action of benzenesulfonyl chloride on the sodium salt of phenylacetylene (30% yield).

Dimethylethynylboronate was prepared in 45% yield from trimethyl borate via ethynylation to sodium ethynyltrimethoxyborate and subsequent reduction to the boronate with BCl_3 .

p-Polyphenyl was prepared by oxidative polymerization of benzene by aluminum chloride-cupric chloride cocatalyst by the method of Kovacic and Kyriakis (2). The reaction ran at 37°C, produced a finely divided light brown solid in 12% yield and free of

inorganic ions. This insoluble powder formed a glossy dark brown pellet when pressed. In a similar manner, a polymeric material was obtained from ferrocene in 0.5% yield. This material, an insoluble brown powder, on pressing produced a glossy black pellet.

3. Radiation Polymerization Studies

Polymerization and copolymerization studies, summarized in Table II, were conducted to define the radiation and thermal sensitivity of the acetylenic monomers and comonomers used (Table I) and to define the type of product produced. Six monomer systems and twelve comonomer systems were used.

TABLE I

STRUCTURAL FORMULAS OF ACETYLENE DERIVATIVES STUDIED

<u>Name</u>	<u>Structure</u>
p-Diethynylbenzene	$\text{HC}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{CH}$
m-Diethynylbenzene	$\text{HC}\equiv\text{C}-\text{C}_6\text{H}_3(\text{C}\equiv\text{CH})-\text{C}\equiv\text{CH}$
Dicyanoacetylene	$\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$
Phenylchloroacetylene	$\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{Cl}$
Propiolic acid	$\text{HC}\equiv\text{C}-\text{COOH}$
Phenylacetylene	$\text{HC}\equiv\text{C}-\text{C}_6\text{H}_5$
Diphenylacetylene	$\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$
N,N-Diethylpropargylamine	$(\text{C}_2\text{H}_5)_2\text{N}-\text{CH}_2-\text{C}\equiv\text{CH}$
Dimethylethynylboronate	$\text{HC}\equiv\text{C}-\text{B}(\text{OCH}_3)_2$
Phenylpropionic acid	$\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-\text{COOH}$

TABLE II

RADIATION-INDUCED POLYMERIZATION OF ACETYLENIC DERIVATIVES

Run	System	Irradiation Conditions				Polymer	
		Time Hr.	Temp., °C	Dose, Megarep	% Yield	G Value Corr.	Uncorr.
9405	p-Diethynylbenzene	45	120	120	32	100	0
12362	"	44	12	17	31	3	7
9423	"	40	-75	-40	28	4	14
12389	m-Diethynylbenzene	47	15	21	33	8	22
9424	Propiolic acid	40	-75	-40	28	5	28
12373	"	50	-73	-32	35	11	50
9422	Dicyanoacetylene	49	17	25	35	3	13
9433	Phenylchloroacetylene	50	120	120	36	98	2
12361	Dimethylethynylboronate	44	12	17	31	3	6
Copolymer Systems							
9404	p-Diethynylbenzene/phenylacetylene	{ 45/49 }	120	120	32	97	0
12352	"	{ 5/95 }	120	120	34	41	0
9417	/diphenylacetylene	{ 50/50 }	120	120	37	86	0
9415	/propiolic acid	{ 51/49 }	120	120	EXPLODED		
9436	"	"	103	103	EXPLODED		
12354	"	{ 54/46 }	12	20	32	82	296
12355	"	{ 5/95 }	120	120	34	82	358
12380	/phenylpropionic acid	(5/95)	6	17	47		
9416	/diethylpropargyl-amine	{ 52/48 }	120	120	37	57	19
12382	"	{ 10/90 }	120	120	33	9	0
9425	/dicyanoacetylene	{ 67/33 }	17	25	35	10	29
9432	/phenylchloro-	"					
9435	"	{ 51/49 }	120	120	EXPLODED		
12374	"	{ 47/53 }	103	103	EXPLODED		
12375	"	{ 52/48 }	10	17	32	9	0
	-dimethylethynyl-boronate	"					
12395	"	{ 49/51 }	10	17	32	40	136
15051	m-Diethynylbenzene	{ 51/49 }	120	120	30	100	3
15052	/diphenylacetylene	{ 8/92 }	20	23	48	4	0
15053	/phenylacetylene	{ 6/94 }	20	23	48	6	26
	/propiolic acid	{ 7/93 }	20	23	48	29	

TABLE III

THERMAL INDUCED POLYMERIZATION OF ACETYLENIC DERIVATIVES

Run	System	Time, Hr.	Temp., °C	Polymer % Yield
12368	p-Diethynylbenzene	69	120	100
12357	"	46	27	0.5
9449	Phenylchloroacetylene	48	120	98
<u>Copolymer Systems</u>				
9406	p-Diethynylbenzene/phenylacetylene {52/48}	45	120	86
12381	" " {22/78}	50	121	70
12369	/diphenylacetylene (50/50)	48	120	94
9437	/propionic acid {52/48}, large tube		105	EXPLODED
9418	" " {55/45}, small tube	52	120	83
9434	/phenylchloroacetylene, small tube	19	110-155	99

As summarized in Table II, the Co-60 gamma-radiation polymerization and copolymerizations of various acetylene derivatives were effected at temperatures varying from -75° to 120°C . Copolymerization systems were investigated at 5 to 50% levels of the diacetylene monomer. Column 1 of this table lists the irradiation time interval; Columns 2 and 3 the temperature range during irradiation; Column 4 the total dose; Column 5 the percentage yield; and Columns 6 and 7 the G values, corrected and uncorrected, respectively. The procedures employed for these radiation-induced polymerizations and product isolations were the same as described in the final report of the preceding study (1). In most cases above ambient temperatures the monomer and comonomer systems underwent both thermal and radiation polymerization. Therefore, controls for most runs were made in the absence of radiation, and the results were used to correct the radiation runs to determine the true radiation yield. Where controls were made, corrected G values are reported in the table. Controls were not made for those systems where uncorrected G values are listed.

The first part of Table II constitutes the results from the homopolymerization runs. At ambient temperatures, polymer yields at dosages of 31 to 35 megareps were low, 3 to 8%, for p-diethynylbenzene, m-diethynylbenzene, dicyanoacetylene, phenylchloroacetylene, and dimethylethynylboronate. At -75° to -40°C , propiolic acid gave much smaller yields and G values than was previously reported. These propiolic acid results are further discussed below.

The effect of temperature on the radiation polymerization of the monomer, p-diethynylbenzene, was investigated from -40° to 120°C (Table II). Above the monomer melting point (96°C), complete polymerization occurred. Controls were conducted for these runs (Table III), and it appears that the 120° polymerization was thermally induced. At and below room temperatures the thermal effects were negligible. Comparison of radiation polymer yields in runs made at and below room temperature showed a small temperature effect. Radiation yields at room temperature ($G = 7$) were $1/2$ of those at -40° to -70°C .

Phenylchloroacetylene also readily underwent thermal polymerization at 120°C in the absence of radiation. Thus the corrected radiation yield ($G = 2$) for the radiation polymerization at 120° was very small, although almost complete polymerization occurred under these conditions.

The second part of Table II summarizes the results from the radiation induced copolymerization of m- and p-diethynylbenzene with propiolic acid, phenylacetylene, diphenylacetylene, N,N-diethylpropargylamine, dicyanoacetylene, phenylchloroacetylene,

and dimethylethynylboronate. The diethynylbenzene comonomers were used as crosslinking agents to insure the formation of solid high molecular weight polymers. Such crosslinking was expected to provide uninterrupted conjugation due to the conjugated groups of the chain bridge. At 50% levels of p-diethynylbenzene sufficient crosslinking occurred to produce solid polymers with propiolic acid, phenylacetylene, diphenylacetylene, and N,N-diethylpropargylamine. Previous radiation studies (1) with these monomers gave syrupy polymers of low molecular weight.

Acetylene derivatives with cyano-, acidic, and basic groups were selected to investigate the effect of these groups and their derivatives on the polymer electrical properties. Conversion of the acid and basic groups of the polymers to various salts and variations of the levels of such groups were expected to produce leads for improving the polymer electrical properties.

As in the case of the homopolymerizations, the copolymerization systems also underwent thermal polymerization. Thus correction of the radiation polymerization runs for the thermal effect (Table III) gave very low radiation yields ($G < 30$) for all but two of the copolymer systems. The exceptions, p-diethynylbenzene/propiolic acid, and p-diethynylbenzene/dimethylethynylboronate, gave G values of 296 and 136, respectively, for the polymerization process.

At 120°C, with and without radiation, chemical yields of copolymers containing 50% diethynylbenzene were above 80% for phenylacetylene, diphenylacetylene, propiolic acid, and m-diethynylbenzene. With N,N-diethylpropargylamine, the yields were 57%. Reduction of the p-diethynylbenzene content from 50% to 10% or less at 120°C, drastically reduced the polymer yields. For example, the polymer yields from p-diethynylbenzene and phenylacetylene was 97% at 50% p-diethynylbenzene levels and only 4.1% at 5% p-diethynylbenzene.

p-Diethynylbenzene copolymerizations were done initially at 120°C to insure homogeneous samples during copolymerization, since the p-diethynylbenzene (m.p. 96°C) is not appreciably soluble in the comonomers below 96°C. Extreme thermal sensitivity of the p-diethynylbenzene copolymer systems at 120°C dictated the use of lower temperatures for carrying out the radiation-induced copolymerizations.

The products which were obtained in the copolymer runs, using about 50% of the p-diethynylbenzene, were dark infusible solids. In order to obtain moldable materials, the percentage of this crosslinking agent was reduced to the 5-10% level. The products in these later instances were either tars or moldable polymers confirming the crosslinking action of the difunctional diethynylbenzene.

Two comonomer systems, p-diethynylbenzene/phenylchloroacetylene and p-diethynylbenzene/propionic acid, were sensitive thermally, exploding at 103°C. Similar results were first observed in the presence of γ -radiation. This is particularly striking since each of the above monomers can be exposed to 120°C alone without exploding. One of these systems, p-diethynylbenzene/propionic acid, yielded 14% gas when heated to 120°C in a thick wall, small bore tube. These results indicate that a sensitization occurs in these systems just above the melting point of the p-diethynylbenzene.

4. Propionic Acid Radiolysis

A number of unsuccessful attempts were made to isolate different low molecular weight products from the radiolysis of propionic acid, to determine why this monomer fails to form much high molecular weight polymer. In previous studies propionic was quite sensitive to radiation, giving high radiation yields of products in the dimer and trimer range. Characterization of the various dimers and trimers via nuclear magnetic resonance was planned. When a sample of propionic acid, radiolyzed at -40° to -70°C, was distilled at 17 mm, and again at 0.5 mm, the only products obtained were starting material and high polymer, the latter representing a yield of 5% or a G value of 28. No explanation can be given for the failure to form dimer and trimer products as was previously observed. It is possible that low level impurities in the propionic acid could account for the difference in dimer-trimer formation in the two sets of radiation-induced polymerizations. In each case, a different batch of freshly distilled propionic acid was used.

5. Chemical and Physical Properties of Acetylene Polymers

The polymer samples isolated from the radiolytic and thermal polymerization of p-diethynylbenzene and copolymers containing 50% p-diethynylbenzene were highly colored red-brown to black glasses. These brittle materials could be readily powdered but resisted pelletization, even under pressures of 10,000 psi at 200°C. These highly crosslinked materials were infusible and insoluble in organic solvents, and the p-diethynylbenzene and p-diethynylbenzene/phenylacetylene polymers showed no signs of decomposition when heated to 300°C. In all cases, no differences were observed between the thermally and radiation produced polymers.

The homopolymers of propionic acid, dicyanoacetylene and phenylchloroacetylene were all black solids. The polypropionic acid and polydicyanoacetylene were soluble in ethanol and the polyphenylchloroacetylene soluble in benzene. The polymer from dimethylethynylboronate was a black tar insoluble in benzene.

Copolymers containing less than 20% p-diethynylbenzene were fusible solids or tars.

All copolymers obtained with low concentration of m-diethynylbenzene were tars.

6. Electrical Properties of Acetylene Polymers

Room temperature resistivity measurements on the solid acetylene derivative polymers and copolymers are summarized in Table IV. Also included in Table IV are resistivity measurements of p-polyphenyl, polyferrocene, and poly-m-terphenyl. The latter was obtained via electron radiolysis of m-terphenyl. Very high, over 10^{10} ohm-cm, resistivity values were obtained in all cases. Thus the polymers are of dubious value for semiconductor use. The highly crosslinked materials, which could not be pressed into pellets, were examined on the bulk glass material obtained directly from the reaction vessel or from powders prepared from these glasses. Where possible, pellets were pressed from the powders and the resistivity values determined on the pellets.

Measurements made on the bulk samples were obtained using point contacts with a Hewlett-Packard volt-meter capable of measuring to 5×10^{10} ohm. In all samples examined, the resistances were higher than could be detected with this instrument. The powders were measured while pressed between two metal disc leads with a megohm bridge as previously described (1). All resistance values obtained near the limit of the instrument (10^{12} ohm-cm) must be considered similar in magnitude.

Copolymers made from p-diethynylbenzene and diethylpropargylamine were soluble in acid and were converted to the HCl salt. No significant reduction in resistivity was observed.

Copolymers of p-diethynylbenzene and propiolic acid were soluble in base and were converted in successive steps from the free acid to the sodium salt, to the free acid, to the potassium salt, to the free acid and finally to the barium salt. No significant changes in the resistivity values occurred in these modifications.

The presence of small quantities of water greatly improved the conductivity of the polyacetylenes. Rigorous drying led to high resistivity values. Polymers reported in the final report of the preceding study (1), having low resistivity values, were carefully dried and subsequent resistivity measurements gave values at and above 5×10^{10} ohm-cm. In some cases, this represented an increase in resistivity by a factor of 10^5 .

TABLE IV

ELECTRICAL PROPERTIES OF ACETYLENIC POLYMERIZATION PRODUCTS

Run	System	History	Resistivity, ohm-cm	
			Bulk	Pellet
9429	p-Diethynylbenzene	Monomer-Control	9.5 x 10 ¹¹	2.9 x 10 ¹¹
9421	"	Thermal polymer from sublimation pot	1.0 x 10 ¹²	
12368	"	Thermal polymer	2.4 x 10 ¹⁰	
9405	"	Irrad. polymer	>5 x 10 ¹⁰	1.8 x 10 ¹²
9433	Phenylchloroacetylene	"	>5 x 10 ¹⁰	>5 x 10 ¹⁰
12379	Dimethylethynylboronate	"	6.2 x 10 ¹⁰	
<u>Copolymer Systems</u>				
12395	p-Diethynylbenzene/m-diethynylbenzene	Irrad. polymer	2 x 10 ¹¹	
9404	/phenylacetylene	"	>5 x 10 ¹⁰	1.4 x 10 ¹²
9406	/	Thermal polymer	1.9 x 10 ¹²	
12381	/	"		6.5 x 10 ¹⁰
9417	/diphenylacetylene	Irrad. polymer	>5 x 10 ¹⁰	1.9 x 10 ¹²
12374	/phenylchloroacetylene	"	1.0 x 10 ¹¹	
12375	/dimethylethynylboronate	"	1.6 x 10 ¹²	2.2 x 10 ¹⁰
9416	/diethylpropargylamine	"	6.7 x 10 ¹⁰	
12382	/	"	>5 x 10 ¹⁰	
9416a	/diethylpropargylamine, HCl salt	"	2.3 x 10 ¹²	1.2 x 10 ¹²
9425	/dicyanoacetylene	"		7.1 x 10 ¹¹
12380	/phenylpropionic acid	"		4.5 x 10 ¹¹
165A	/propionic acid, sodium salt, methanol soluble	"		
165B	/propionic acid, sodium salt, methanol insoluble	"		
165C	/propionic acid, free acid from 165 A and B	"	8 x 10 ¹⁰	
165D	/propionic acid, potassium salt	"	5 x 10 ¹¹	
165E	/ " , free acid from 165D	"	1.0 x 10 ¹⁰	
165F	/ " , barium salt	"	8 x 10 ¹⁰	
<u>Polyaromatics</u>				
12393	p-Polyphenyl			1.5 x 10 ¹¹
12397	Polyferrocene			5 x 10 ¹⁰
12398	"			2 x 10 ¹⁰
12386	"			6.5 x 10 ¹⁰
15060	"			1.5 x 10 ¹⁰
12359	Poly-m-terphenyl		1.4 x 10 ¹⁰	>5 x 10 ¹⁰

Resistivity values of two p-polyphenyl and one polyferrocene pellets were measured with increasing temperature up to 300°C. As shown in Table V, the expected reduction in resistivity with increasing temperature occurred, but no large breaks in the over-all trend were observed. The 300°C resistivities were of the order of 10^7 to 10^8 ohm-cm.

TABLE V

EFFECT OF TEMPERATURE ON RESISTIVITY MEASUREMENTS

<u>Temp.</u>	<u>Polyphenyl</u>	<u>Resistivity Values, ohm-cm</u>	
		<u>Polyphenyl</u>	<u>Polyferrocene</u>
28		5×10^{11}	
38			2×10^{10}
58		3×10^{11}	
78			4.4×10^9
88		1.5×10^{11}	
98			1.7×10^9
108			
118		8.2×10^{10}	
128	1.6×10^{11}		4.8×10^8
138			
148		4.0×10^{10}	
158	1.4×10^{10}		2.1×10^8
168			
178		1.5×10^{10}	
188	6.8×10^9		7.9×10^7
198			
208	4.0×10^9	4.5×10^9	4.6×10^7
218			
228			2.2×10^7
238	1.7×10^9	1.2×10^9	
248			
258			
268	7.8×10^8	3.8×10^8	8.8×10^6
278			
288			
298		7.0×10^8	8.5×10^6
300	6.6×10^8	6.1×10^8	1.2×10^7

B. EXPERIMENTAL

1. Chemical Synthesis

a. p-Diethynylbenzene p-Diethynylbenzene was prepared from divinylbenzene via bromination followed by dehydrobromination (3). Bromine (650 g, 4.1 moles) was added slowly (1.5 hr) with stirring to a cooled solution of 375 g of mixed divinylbenzenes (2.9 moles) in 600 ml chloroform. The divinylbenzene was a mixture of isomers, mostly meta- and para-, obtained from the Borden Co. The solution was maintained at about 5°C during the bromine addition. Stirring was continued for an additional 3/4-hr at 5°C and the voluminous precipitate was separated by filtration. The white solids were washed with 40 ml of cold chloroform and pressed dry. Recrystallization from 500 ml chloroform gave 97.4 g of 1,4-bis-(1,2-dibromoethyl)benzene, m.p. 156-158°C (7.5% yield).

Fifty grams (0.11 mole) of the 1,4-bis-(1,2-dibromoethyl)benzene was added to a refluxing solution of 18 g (0.46 mole) of potassium in 1 liter of t-butanol. After 1 hr stirring, the mixture was allowed to cool to room temperature and diluted to 4 liters with ice water. Filtration gave 8.8 g of p-diethynylbenzene, m.p. 94°C (63% yield). The product became yellow-brown on standing. Sublimation at 90-100°C under reduced pressure gave a colorless product, m.p. 95°C.

b. m-Diethynylbenzene m-Diethynylbenzene was similarly prepared from m-divinylbenzene via bromination followed by dehydrobromination. Bromination of the mixed divinylbenzenes and separation of the solid 1,4-bis-(1,2-dibromoethyl)benzene as described above left a chloroform filtrate of 1,3-bis-(1,2-dibromoethyl)benzene and some dibromodiethylbenzenes. While large scale distillations of this solution gave only tars, repeated distillations on a small scale (10-15 g) yielded viscous syrups from which the 1,3-bis-(1,2-dibromoethyl)benzene, m.p. 65°C, could usually be crystallized when triturated with cold ethanol.

1,3-Bis-(1,2-dibromoethyl)benzene, 12.5 g (0.027 mole) was added to a refluxing solution of 4.5 g (0.11 mole) of potassium in 250 ml of t-butanol. After 1 hr of stirring, the mixture was allowed to cool to room temperature and diluted to 1 liter with ice water. The product was extracted with ether, and after drying, was distilled to yield 1.5 g m-diethynylbenzene, b.p. 80°C (16 mm) n_D^{25} 1.5720.

c. Dicyanoacetylene Using the procedure of Blomquist and Winslow (4), acetylenedicarboxamide was prepared by the careful addition of 50 g dimethyl acetylenedicarboxylate (0.35 mole) to a vigorously stirred 200 ml concentrated ammonia solution cooled to -10°C . Stirring was continued one hour longer. The precipitated amide was filtered, washed with 20 ml ethanol, and dried 4 days in a vacuum desiccator. A 31.4 g (80%) yield of the dry amide, m.p. 195°C , was obtained.

An intimate mixture of 6 g dry acetylenedicarboxamide, 100 g dried sea sand, and 50 g phosphorus pentoxide was prepared, divided equally into four portions, and added to 2.1 x 22 cm test tubes. These tubes were attached in a vertical position to a common horizontal manifold which led to a dry ice-cooled receiver. The entire system was flushed with dry nitrogen, evacuated, and closed. The four test tubes were heated with a wax bath at 212°C , and within 15 minutes the product was collected in the dry ice-cooled receiver. Upon thawing, the product darkened and 0.44 g (11% yield) was distilled immediately into a break seal tube for irradiation.

d. Phenylchloroacetylene Phenylchloroacetylene was prepared by the action of benzenesulfonyl chloride on sodium phenylacetylide using the method of Truchet (5). Eleven grams of sodium amide, washed with ethyl ether, was charged to a 1-liter flask with 500 ml of ethyl ether. Phenylacetylene, 16 g, was added dropwise to the stirred mixture. The solution was refluxed 3 hr and 60 ml of ether was distilled to remove the last traces of ammonia. To this solution, containing a large amount of light-brown solids, was added dropwise 30 g of benzenesulfonyl chloride and refluxing was continued for 2-3/4 hr. The ether solution was washed with ice water, dried with magnesium sulfate, and the ether removed by distillation. The crude pale-green product, weighing 6.1 g, 29%, was distilled at $71-78^{\circ}\text{C}$ at a pressure of 16 torr, n_D^{25} 1.5760.

e. Dimethylethynylboronate Using procedure of Willcockson (6), dimethylethynylboronate was prepared from trimethyl borate.

Sodium acetylide was prepared by the procedure of Rutledge (7). In a 3-neck 500-ml flask, equipped with a high speed mechanical stirrer and condenser, was charged 50 ml of xylene, 50 g of sodium, 0.13 g pyridine, and 0.25 g oleic acid. After flushing the system with dry nitrogen, the xylene was heated to 105°C and stirred at high speed for eight minutes. The resulting gray dispersion was cooled without stirring.

This sodium dispersion, 11.5 g, and 600 ml of dry xylene was placed in a 3-neck 1-liter flask equipped with a mechanical stirrer, condenser and bubbler. The mixture was heated to 105°C with stirring and then acetylene bubbled through the solution for 1.5 hr.

To the sodium acetylide prepared above, in the same flask and kept under a nitrogen atmosphere, was added 59.6 g of trimethyl borate (0.57 mole) with rapid stirring at room temperature. The mixture was then heated to 105°C for 45 minutes. While maintaining the temperature at 5-10°C with an ice bath, 14 g (0.17 mole) of liquid boron trichloride was added dropwise over a 30 minute period. The mixture was stirred an additional 15 minutes at 5-10°C and 1.5 hr at 10-25°C. Solids were removed by filtration under nitrogen and the filtrate was distilled in a nitrogen atmosphere. The dimethylethynylboronate, b.p. 56-58°C and 245 mm Hg pressure (lit. 59-62/262 mm), was obtained in 45% yield.

f. p-Polyphenyl Benzene was polymerized at room temperature under a nitrogen atmosphere to p-polyphenyl, using the procedure of Kovacic and Kyriakis (2). To a 500-ml flask equipped with a stirrer, was added in order 78.1 g (1 mole) of benzene, 1 ml of water dropwise, 66.7 g (0.5 mole) of anhydrous aluminum chloride and 67.2 g (0.5 mole) of anhydrous cupric chloride. The temperature was raised to 37°C, and the reaction allowed to proceed for 30 min. The reaction mixture was then added to water and filtered. After treating with 18% hydrochloric acid and filtering, the solid product was triturated 3 times with boiling concentrated hydrochloric acid and washed with water until the washings were colorless. After two triturations with boiling 2 molar sodium hydroxide, water washings were continued until the filtrate was colorless. Then the polymer was washed repeatedly with distilled water until the filtrate gave a negative test for chloride ion with silver nitrate. Vacuum drying at 140°C for 5 hr gave 4.5 g, a 12% yield of polyphenyl, a brown infusible insoluble solid.

g. Polyferrocene Using the procedure described above for p-polyphenyl, several attempts were made to prepare polyferrocene from ferrocene. To a 3-necked flask equipped with a stirrer, was added, in order, 50 ml cyclohexane, 62.1 g (0.33 mole) ferrocene, 22.0 g (0.17 mole) aluminum chloride, 1/2 ml H₂O dropwise, and 22.2 g (0.17 mole) cupric chloride. This mixture, which contained considerable solids, was stirred for 1 hr at 50°C, cooled and added to 150 g of ice. The solids were filtered, washed with 100 ml of 18% hydrochloric acid, triturated 3 times with boiling concentrated hydrochloric acid, and washed with water. The solid remaining, 28.7 g, was mostly starting material. Cyclohexane extraction in a Soxhlet apparatus

removed the starting material, yielding 0.3 g of polyferrocene, a black insoluble infusible powder. The material was used as such for electrical measurements.

A similar run, irradiated with γ -rays to a dose of 3×10^7 r, yielded on isolation 0.2 g of a similar black insoluble, infusible solid.

A third run, similar to the irradiated one described just above, except containing no aluminum chloride and receiving 47×10^6 r of γ -radiation, yielded 0.2 g of black solid.

h. Attempted syntheses The following syntheses were attempted unsuccessfully:

- (1) o-Cyanophenylpropionic acid and o-cyanophenylacetylene from o-cyanocinnamic acid.
- (2) Phenylcyanoacetylene from phenylacetylene and cyanogen bromide.
- (3) Diethynylantracene from anthraquinone.

2. Sample Preparation

The irradiations were conducted in glass break-seal tubes described in the Final Report on "Radiation Polymerization of Acetylene Derivatives", 10 August 1962, Contract No. NObs-86072 (1). The samples, 1 to 2 g scale, were irradiated under vacuum with a 500-curie Co-60 gamma-ray source. Dose rates of 0.7 megarep/hr and total dosages of about 30 megarep were used. Polymer yields varied from 3 to 100%.

3. Evaluation

Where possible, the initial monomer was distilled from the residue and the residue weight was reported as polymer. Visual, chemical and physical observations were made on the resulting polymers.

Electrical resistivity measurements were made on all solid polymers. Where possible, the solids were prepared into pellets for electrical measurements. Infusible solids were evaluated as powders. Before attempting to press the samples into pellets, each solid polymer was tested for shock and pressure sensitivity with an impact tester.

4. Equipment

The equipment used was described in the Final Report on "Radiation Polymerization of Acetylene Derivatives", Contract No. NObs-86072 (1). The equipment included: (1) a vacuum-line for sample preparation and purification, loading irradiation vessels, and working up of radiolyzed materials; (2) an irradiation chamber to hold vessels for Co-60 γ -radiolysis; (3) a Co-60 gamma-irradiator; (4) an impact tester to determine the pressure and shock sensitivity of the acetylene derivative polymers; (5) a pellet press; (6) a sample holder for pellet and powder resistivity measurements; and (7) the electrical equipment needed for resistance measurements.

IV. CONCLUSIONS

1. Polymers produced via the radiolysis or pyrolysis of acetylene derivatives have very high resistivity values (over 10^{10} ohm-cm).
2. Trace quantities of water in polymers produced from acetylene derivatives, containing polar groups, reduces the resistivity values several orders of magnitude below that of the dry material.
3. Resistivity values of acetylene derivative polymers, containing carboxyl and amine groups, are essentially unaltered by conversion of these groups to various metal and acid salts, respectively.
4. Acetylene derivatives will polymerize with heat or radiation and the sensitivity to polymerization varies widely.
5. A carboxyl group substitution on an acetylene carbon sensitizes the molecule to radiation induced polymerization.
6. Diethynylaromatics function as a cross-linking agent when used with monoacetylene derivatives in thermal and radiolytic copolymerizations.
7. p-Diethynylbenzene sensitizes the thermal and radiolytic polymerization of specific acetylene derivatives.

V. RECOMMENDATIONS

1. A study directed to establish if a known polyene has good electrical conductivity and the relationship of electrical conductivity vs. chain length.
2. Development of a method for preparing a model polyene by facile chemical means to insure complete polyene character.
3. Development of a method to define the polyene character of a polyene.
4. Investigate the properties and preparation of the same model polyene via radiolysis of the corresponding acetylene derivative to establish the feasibility of radiolytic synthesis of a complete polyene.

VI. REFERENCES

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